Bull. Inst. Chem. Res., Kyoto Univ., Vol. 54, No. 6, 1976

LABORATORY OF CERAMIC CHEMISTRY

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Researches on ceramic science were taken up by Professor Ikutaro Sawai and his associates in the institute in 1937. The research items first chosen were special glasses (optical glasses) and glass fibers. In 1958, Professor Megumi Tashiro succeeded Professor Sawai as the head of the laboratory. In 1964, the laboratory was officially named as Laboratory of Ceramic Chemistry. The researches made since 1958 deal with basic problems in ceramic science, especially of glasses, glass-ceramics, sintered ceramics and fused ceramics. The main stress has been laid on elucidation of relations between microstructures of these materials and their properties, which would lead to discovery of new ceramics. The major researches made since 1967 are outlined hereunder.

I. Crystallization of Glasses

Mechanism of crystallization of glasses by heat-treatment, and properties of the resultant crystallized glasses were investigated. The compositions of the glasses examined were of the Li_2O-SiO_2 system and those from which ferroelectric crystals were precipitated. The findings are summarized as follows: a) The extremely high rate of nucleation in the $Li_2O \cdot 2SiO_2$ glass is attributed to the big change in free energy associated with bulk transformation of glass into crystal. b) Mechanical strengths of crystallized glasses and phase-separated glasses increase with decreasing size of the constituent crystal grains and the phase-separated glassy droplets, respectively. The strength of the formers is further increased by the formation of a glassy layer with low thermal expansion coefficients. c) Addition of Al_2O_3 together with SiO_2, both in limited amounts, respectively, to the components of ferroelectric crystals is effective in producing transparent ferroelectric crystallized glasses. d) Dielectric constant of the $PbTiO_3$ crystallized glasses show two maxima at 0.15 μm and 25 nm of size of the constituent $PbTiO_3$ crystals, which are explained in terms of internal stress and internal electric field, respectively.

II. Crystallization of Melts

Methods for fabrication of inorganic and non-metallic polycrystalline aggregates from their melts by simple casting or unidirectional solidification, and properties of the resultant ingots were investigated. The findings are summarized as follows: a) When a melt is solidified unidirectionally in a crucible, a layer of sintered ceramics or glass-ceramics previously placed or applied on the inner surface of the bottom of the crucible acts as crystal seeds which fascilitate growth of a stable crystal phase, leading to the formation of a well-oriented, fine-grained, polycrystalline aggregate. b) Formation of bubbles in viscous Li_2O-SiO_2 melts during their solidification can be avoided by lowering the solidification rate to a certain degree. The bubble formation is attributed to the high viscosity of the melts and the big difference in solubility of gas between the melt and crystal phase. c) The 0.7 $NaNbO_3$·0.3 $BaTiO_3$ melt, when solidified unidirectionally at a slow rate, forms a transparent polycrystalline aggregate showing a high electro-optic effect.

III. Structure and Properties of Special Glasses

Glass-forming tendency of aluminate melts containing no simple glass-forming oxide such as SiO_2, B_2O_3, P_2O_5, and GeO_2, and properties of their glasses were investigated. New families of aluminate glasses showing high infrared transmissions were obtained on a practically useful scale from ternary systems (Na_2O, K_2O or BaO)-TiO_2–Al_2O_3 and (K_2O or Cs_2O)-(Nb_2O_5 or Ta_2O_5)-Al_2O_3.

IV. Photochromism of Glassy and Crystalline Oxides

Photochromism of glasses containing silver halides were investigated in relation to their manufacturing conditions and microstructures. Phototropic behavior of alkaline earth tungstates were investigated in relation to their composition. $CaWO_4$, $SrWO_4$, $BaWO_4$, and their solid solutions prepared by solid state reaction showed strong phototropy when doped with a small amount of Bi.

V. Glassy State

The ratio of glass transition temperature to the liquidus temperature was found to be 2/3 for a wide variety of inorganic glass forming systems including the elements, oxides and sulfides and technologically important systems such as borates and silicates. Coordination number of Al was investigated for a wide variety of oxide glasses by X-ray emission spectroscopy.

VI. High Pressure Effects on Glasses

Powders of Co- or Ag-containing or γ-irradiated glasses were compressed at 10–65 Kbar with a simple squeezer apparatus, and the effects of compression on their light absorption spectra, density, and crystallization tendency were investigated.

VII. Special Ceramics

Addition of glass powders rich in BaO and TiO_2 to $BaTiO_3$ crystal powders was found to be effective to extend the firing range of $BaTiO_3$ ceramics, without giving no detrimental effect on their dielectric properties. Adsorption of heavy metal ions in aqueous solutions to powder compacts of various hydrooxides such as $Ca_6Si_6O_{17}(OH)_2$ and $CaHPO_4 \cdot 2H_2O$, were investigated in relation to their compositions and microstructures.

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(* indicates an article published in Japanese)

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